

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

N-oxide bridged manganese(II) coordination polymers

Rupam Sarma^a; Alagarsamy Perumal^b; Jubaraj Bikash Baruah^a

^a Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, India ^b Department of Physics, Indian Institute of Technology Guwahati, Guwahati, India

To cite this Article Sarma, Rupam , Perumal, Alagarsamy and Baruah, Jubaraj Bikash(2009) '*N*-oxide bridged manganese(II) coordination polymers', Journal of Coordination Chemistry, 62: 9, 1513 — 1524

To link to this Article: DOI: 10.1080/00958970802621504

URL: <http://dx.doi.org/10.1080/00958970802621504>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

N-oxide bridged manganese(II) coordination polymers

RUPAM SARMA[†], ALAGARSAMY PERUMAL[‡] and JUBARAJ
BIKASH BARUAH*[†]

[†]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, India

[‡]Department of Physics, Indian Institute of Technology Guwahati, Guwahati, India

(Received 9 April 2008; in final form 5 August 2008)

A simple method for synthesis of manganese(II) coordination polymers with different benzoate ligands and pyridine *N*-oxide having general composition $[\text{Mn}(\text{RC}_6\text{H}_4\text{CO}_2)_2(\text{PyO})]_n$ is presented (where PyO = pyridine *N*-oxide and R = H, **1a**; R = 4-NO₂, **1b**; R = 4-Cl, **1c**; R = 4-OH, **1d**; R = 2-NO₂, **1e**). All these polymers are characterized by X-ray crystallography and other spectroscopic techniques. The coordination polymers have similar structures, but the positions of the manganese atoms differ. For example, **1c** is highly symmetric and a mirror plane exists between each manganese site (2/m). In **1d**, the manganese centers are related by an inversion center (-1) whereas in **1e** the manganese centers are related by C₁ rotation (1). Reaction of manganese(II) acetate tetrahydrate with 4-chlorobenzoic acid and PyO upon crystallization from methanol/pyridine gave crystals of coordination polymer **1c** along with aqua-*bis*-pyridine *bis*-4-chlorobenzoato manganese(II) (**2**). The structure of **2** also determined by single-crystal X-ray diffraction has a 1-D hydrogen bonded chain structure. Temperature-dependent zero-field cooled and field-cooled magnetization data of **1a–1c** measured at 20 Oe and 1000 Oe show field-dependent magnetization spread over a wide temperature range from 5 to 300 K. These coordination polymers show anti-ferromagnetic behavior below 20 K.

Keywords: Coordination polymer; Manganese; Pyridine *N*-oxide; Carboxylates; Weak interactions; Field-dependent magnetization

1. Introduction

Molecular magnets are of interest in material science and design requires understanding at the molecular level [1]. Transition metal complexes with *N*-oxide ligands are important in magneto-chemistry [2]; a large number of reports dealing with magnetic properties of low nuclearity complexes are available [3]. Magnetic properties of polymeric systems have much interest [3, 4] but it is difficult to find well-defined polymeric systems that can be prepared by simple synthetic pathways. We have shown two examples of the 1-D polymers of manganese(II) with *N*-oxide ligands that could be easily prepared [5]. In this study, we describe the general synthetic pathway along with field-dependent magnetization properties of a few manganese(II) 1-D coordination polymers containing pyridine *N*-oxide (PyO). We also describe a manganese pyridine complex, which can be converted to the PyO complex through ligand exchange.

*Corresponding author. Email: juba@iitg.ernet.in

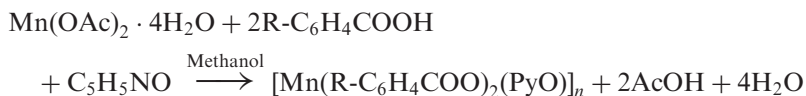
Table 1. Characteristic IR frequencies of the manganese complexes.

Coordination polymers	IR frequency (cm ⁻¹) and assignment
[Mn(4-C ₆ H ₅ CO ₂) ₂ (PyO)] _n (1a)	1593 ν _{as} (CO ₂), 1397 ν _s (CO ₂), 1219 (N–O _{str}), 549 (Mn–O _{str})
[Mn(4-NO ₂ C ₆ H ₄ CO ₂) ₂ (PyO)] _n (1b)	1580 ν _{as} (CO ₂), 1343 ν _s (CO ₂), 1208 (N–O _{str}), 543 (Mn–O _{str})
[Mn(4-ClC ₆ H ₄ CO ₂) ₂ (PyO)] _n (1c)	1597 ν _{as} (CO ₂), 1399 ν _s (CO ₂), 1218 (N–O _{str}), 529 (Mn–O _{str})
[Mn(4-OHC ₆ H ₄ CO ₂) ₂ (PyO)] _n (1d)	3299 (O–H _{str}), 1552 ν _{as} (CO ₂), 1391 ν _s (CO ₂), 1205 (N–O _{str}), 546 (Mn–O _{str})
{[Mn(2-NO ₂ C ₆ H ₄ CO ₂) ₂ (PyO)] _n }·2H ₂ O (1e)	3504(O–H _{str}), 1602 ν _{as} (CO ₂), 1402 ν _s (CO ₂), 1224 (N–O _{str}), 533 (Mn–O _{str})
[Mn(4-ClC ₆ H ₄ CO ₂) ₂ (Py) ₂ H ₂ O] (2)	3402(O–H _{str}), 1587 ν _{as} (CO ₂), 1407 ν _s (CO ₂), 532 (Mn–O _{str})

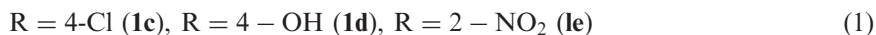
2. Results and discussion

2.1. Synthesis and characterization of the coordination polymers

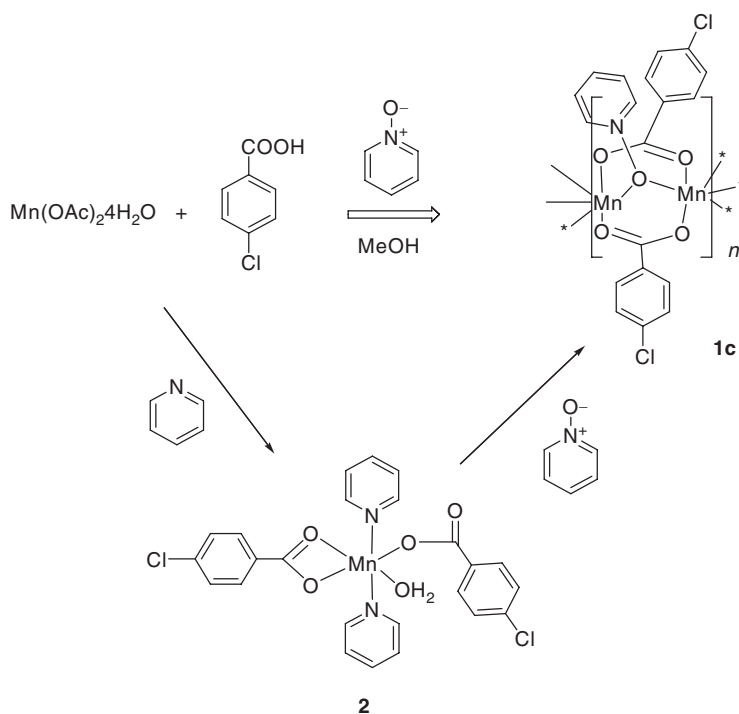
One-dimensional coordination polymers of manganese(II) can be prepared by a very simple reaction of manganese(II) acetate tetrahydrate with an aromatic carboxylic acid and PyO [equation (1)] in a one pot reaction.



where R = H (**1a**), R = 4-NO₂ (**1b**),



The reaction is general and various coordination polymers can be prepared by this route. All the coordination polymers have characteristic IR frequencies from the carboxylate group and the *N*-oxide. The asymmetric stretching of the carboxylates are observed in the range 1600–1550 cm⁻¹ with the symmetric stretching at 1400 cm⁻¹. The N–O stretching of the PyO is at 1220 cm⁻¹. Mn–O stretching frequencies are near 540 cm⁻¹. Characteristic IR frequencies of the complexes are tabulated in table 1. Molar conductances of the polymers are in the range of 40–60 S cm² mol⁻¹ in methanol, suggesting nonionic nature. The structures of **1a** and **1b** were reported recently [5]. Coordination polymer **1c** prepared from 4-chlorobenzoic acid and manganese(II) acetate tetrahydrate and PyO could not be crystallized from methanol but could be crystallized from pyridine. A mononuclear complex, aqua-bis-pyridine bis-4-chlorobenzoato manganese(II), **2**, crystallizes initially, which on re-dissolution in the residual solution gives **1c**. Thus, it can be suggested **1c** when dissolved in pyridine gives a mononuclear complex initially, which further reacts with PyO to give the coordination polymer. The reaction is shown in scheme 1. Complex **2** can also be prepared in high yield by reacting manganese(II) acetate tetrahydrate with 4-chlorobenzoic acid and pyridine (py). The characteristic N–O stretching frequency at 1217 cm⁻¹ is observed for **1c**, but absent in **2**. Polymer **1c** is thermally stable to 280°C, where it loses PyO (wt loss, theoretical 20.62%, found 19.39%); **1c** has a highly symmetric structure and crystallizes in the orthorhombic space group *Cmcm*. The asymmetric unit is shown in figure 1(b). The manganese centers are nearly octahedral with four equivalent Mn1–O1 bonds from bridging carboxylates and two Mn1–O2 bonds from bridging PyO. The polymeric chain grows uniformly along the *c*-crystallographic axis as shown in figure 1(a). The bond



Scheme 1. The reaction of manganese(II) acetate tetrahydrate with 4-chlorobenzoic acid and pyridine N-oxide.

distances (\AA) are Mn1–O1, 2.14(1); Mn1–O2, 2.20(1) and bond angles ($^\circ$) are $\angle \text{O1–Mn1–O1}$, 87.26(6) and $\angle \text{O1–Mn1–O2}$, 89.01(4). In this complex, $\text{Mn} \cdots \text{Mn}$ bond distances are 3.74 \AA . In dinuclear aqua and carboxylate-bridged complexes such separations are in the range 3.65–3.75 \AA [6]. Complex **2** has a chelating as well as monodentate 4-chlorobenzoate ligand along with an aqua and two pyridines [figure 2(a)] in a distorted octahedral geometry with pyridines *trans*. The complex self-assembles in the solid state through intermolecular hydrogen bonding of the aqua of one molecule with two carboxylate oxygens of an adjacent molecule [figure 2(b)]. The hydrogen bonding parameters are $d_{\text{D} \cdots \text{A}}$ (\AA), $\text{O5–H} \cdots \text{O4}$, 2.74; $\text{O5–H} \cdots \text{O2}$, 2.64; and $\angle \text{D–H} \cdots \text{A}$ ($^\circ$), $\angle \text{O5–H} \cdots \text{O4}$, 167.43; $\angle \text{O5–H} \cdots \text{O2}$, 161.96. In this solid state self-assembly the Mn–Mn separation is 5.93 \AA .

Complex **2** has a magnetic moment without diamagnetic correction 5.53 BM at room temperature. Both **1c** and **2** show only a broad esr signal at $g=2.005$ and $g=2.012$, respectively, in solid state at room temperature without any hyperfine structure (Supplemental Material). At liquid nitrogen temperature we did not see any significant difference.

Coordination polymer **1d** is obtained in high yield and, despite having a phenolic OH and manganese, it is very stable; **1d** crystallizes in the space group *Pbcn* and possesses a highly symmetric structure as shown in figure 3(a) and (b) with distorted octahedral geometry around manganese connected by N-oxide and carboxylate bridges. The O–H groups participate in layer formation through intermolecular hydrogen bonding interactions.

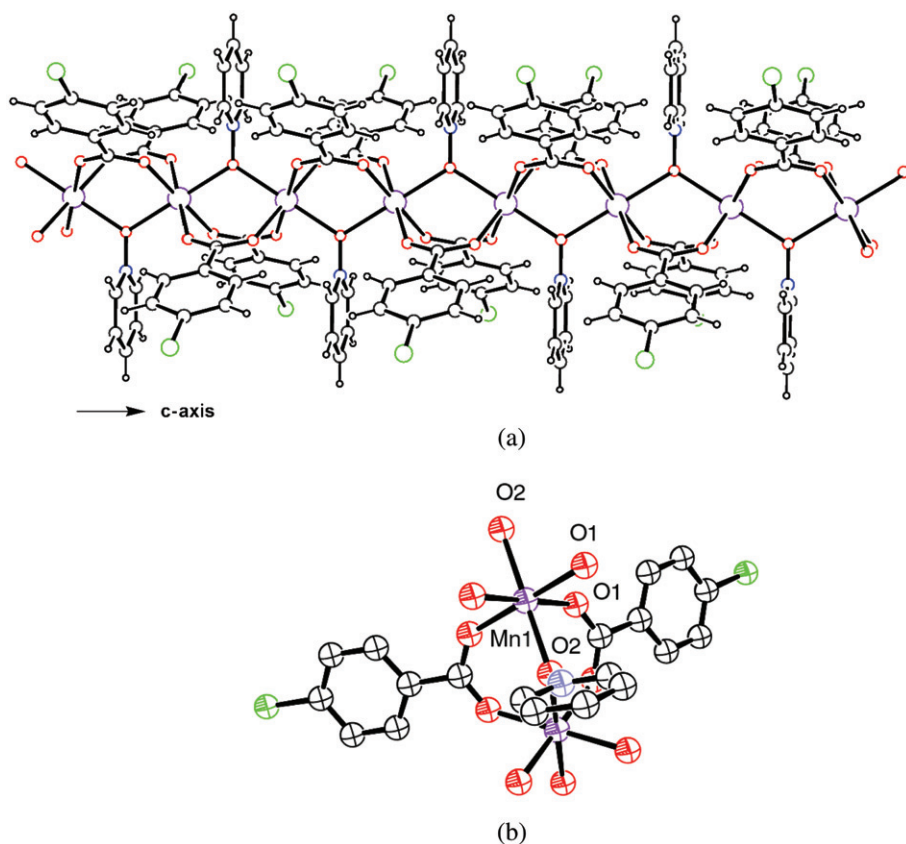


Figure 1. (a) Structure of coordination polymer **1c**. (b) The asymmetric unit in unit cell of the structure (drawn with 50% thermal ellipsoid).

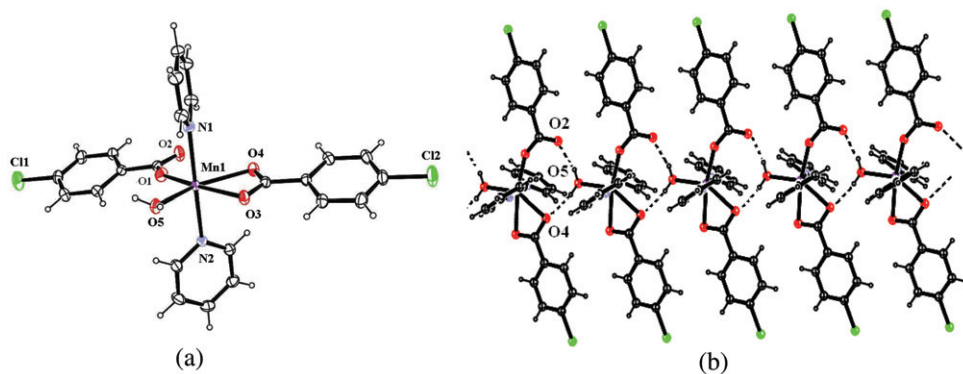


Figure 2. (a) Structure of aqua-*bis*-pyridine *bis*-4-chlorobenzoate manganese(II) (**2**) and (b) hydrogen-bonded self-assembly of **2**. Selected bond distances (Å) and angles (°) Mn1–O1, 2.05(15); Mn1–O5, 2.13(1); Mn1–O3, 2.26(1); Mn1–N1, 2.27(1); Mn1–N2, 2.29(1); Mn1–O4, 2.29(14); <O1–Mn1–O5, 98.69(7); <O1–Mn1–O3, 168.55(6); <O5–Mn1–O3, 92.41(6); <O1–Mn1–N1, 90.43(6); <O5–Mn1–N1, 91.05(6); <O3–Mn1–N1, 92.16(6); <O1–Mn1–N2, 85.76(6); <O5–Mn1–N2, 93.13(6); <O3–Mn1–N2, 90.88(6); <N1–Mn1–N2, 174.73(6); <O1–Mn1–O4, 111.51(6); <O5–Mn1–O4, 149.67(6); <O3–Mn1–O4, 57.60(5); <N1–Mn1–O4, 86.10(6); <N2–Mn1–O4, 91.89(6).

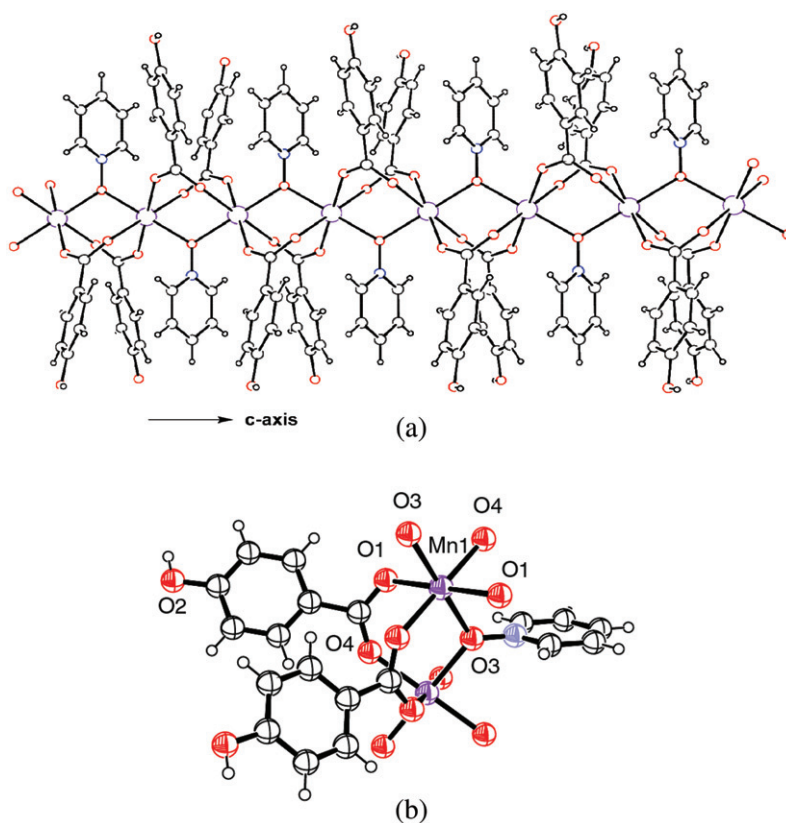


Figure 3. (a) Structure of coordination polymer **1d** and (b) the asymmetric unit in unit cell of the structure **1d**. Selected bond distances (Å) and angles ($^{\circ}$) are Mn1–O4, 2.11(1); Mn1–O3, 2.21(9); Mn1–O1, 2.24(1); \angle O4–Mn1–O4, 180.0; \angle O4–Mn1–O3, 87.21(5); \angle O4–Mn1–O3, 92.79(5); \angle O3–Mn1–O3, 180.0; \angle O3–Mn1–O1, 91.96(4).

Coordination polymer **1e** is prepared as the dihydrate [figure 4(b)] with distorted octahedral manganese. We could not locate hydrogens in one water molecule due to poor quality of the crystals; nevertheless, we obtained a satisfactory structure.

Although the coordination polymers have similar structures, the symmetries of the manganese atoms differ. For example, **1c** is highly symmetric with a mirror plane between each manganese ($2/m$). In **1d**, the manganese centers are related by -1 symmetry and in **1e** these are related by one symmetry.

2.2. Magnetic properties of the coordination polymers

The magnetization data for the zero-field cooled (ZFC) sample and field-cooled sample (FC) were measured at two different external applied fields, 20 Oe and 1000 Oe for **1a–1c**. Under both conditions, these coordination polymers show a magnetic phase transition from paramagnetic to anti-ferromagnetic at about 20 K. As an illustrative case field-dependent magnetization plots for **1c** are shown in figures 5(a) and (b). Similar variation in magnetic properties for **1a** and **1b** are given as Supplementary Material.

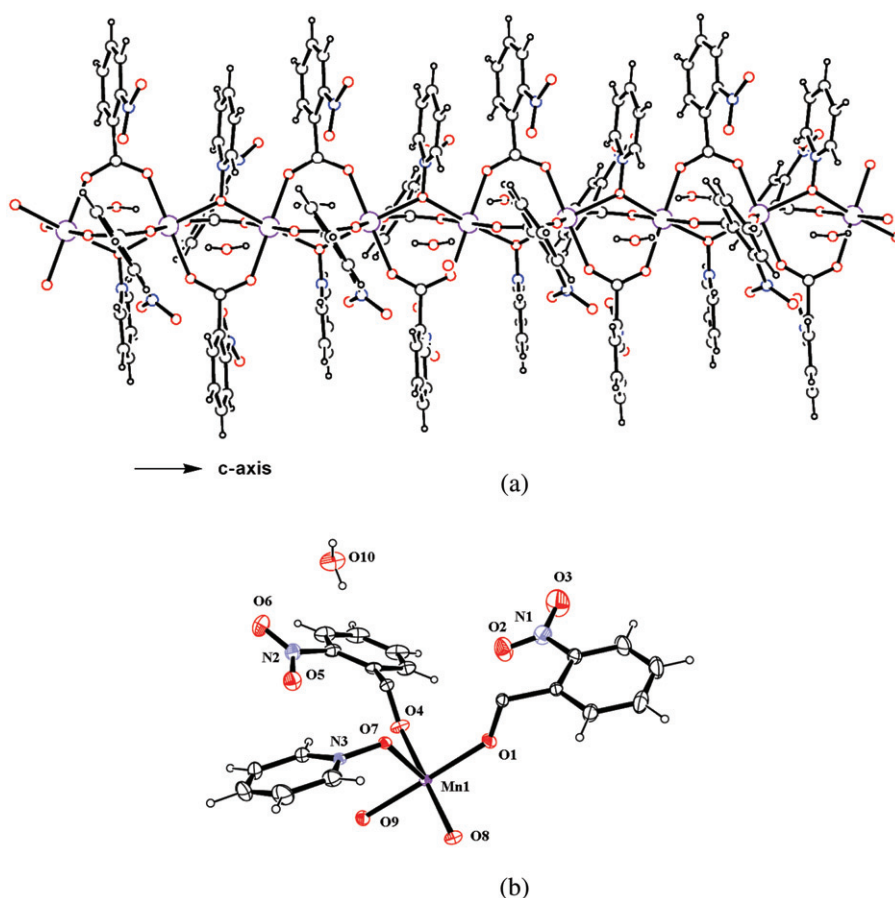


Figure 4. (a) Structure of coordination polymer **1e** and (b) the smallest asymmetric unit in unit cell of the structure **1e**. Selected bond distances (Å) and angles ($^{\circ}$) Mn1–O9, 2.11(2); Mn1–O1, 2.11(2); Mn1–O8, 2.19(2); Mn1–O4, 2.20(2); Mn1–O7, 2.23(2); <O9–Mn1–O1, 179.20(9); <O9–Mn1–O8, 92.58(1); <O1–Mn1–O8, 87.66(1); <O9–Mn1–O4, 87.63(1); <O1–Mn1–O4, 92.13(1); <O8–Mn1–O4, 179.74(9); <O9–Mn1–O7, 88.03(8); <O1–Mn1–O7, 91.20(9); <O8–Mn1–O7, 91.68(8); <O4–Mn1–O7, 88.49(8).

The nature of the temperature-dependent magnetization curves depends on the applied field conditions. In 1000 Oe [figure 5(b)], no clear distinction between the FC and ZFC magnetization data was observed, even at the phase transition region. On the other hand, in 20 Oe [figure 5(a)], the FC magnetization data show substantial enhancement of magnetization over the ZFC condition from 5 to 300 K. This suggests that the low field FC measurement causes additional magnetization adding to the ZFC condition. These observations are unique as 2-D coordination polymers of manganese(II) show ferroelectric properties [4a] and, to the best of our knowledge, observation of the field-dependent properties at low temperature has not been observed in 1-D manganese coordination polymers. Field-induced magnetization of a 1-D nickel complex suggested weak interactions in such behavior [7a]. Field-dependent magnetization properties at low temperature in nano-particles of manganese dioxide [7b] resulted from enhanced anti-ferromagnetic ordering of manganese nanoparticles [7b]. In **1a–1c** the Curie–Weiss-type behavior could be seen in the temperature range of 100–300 K. Least-squares fitting was

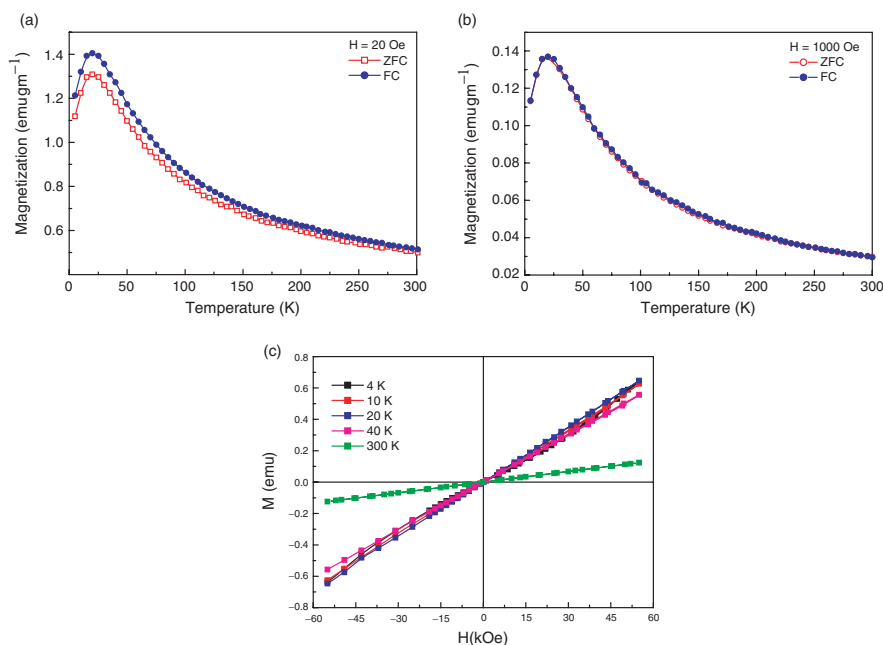


Figure 5. Temperature-dependent ZFC (open circles) and FC (closed circles) magnetization data of **1c** measured at (a) 20 Oe, (b) 1000 Oe, and (c) plot of field vs. magnetization at different temperature for **1c**.

carried out for magnetic susceptibility values with temperature by using the equation $\chi = [C/(T-\theta)] + \chi$ (dia) giving $C = 0.03396, 0.02106, 0.02686$; $\theta = -473 \text{ K}, -459 \text{ K}, -444 \text{ K}$; and χ (dia) $= -0.000002, -0.000003, -0.000001 \text{ emu g}^{-1}$, respectively, for **1a**, **1b**, and **1c**. The θ values are reasonable for anti-ferromagnetic metal carboxylate complexes [8]. Coordination polymers **1d** and **1e** have magnetization of 1.025 and 0.837 emu g^{-1} at 20 Oe at 293 K.

Structures of **1a–1e** show chain structures that are weakly interacting through C-H \cdots O and C-H \cdots π interactions in lateral directions. The 1-D structure of **1a** and its self-assembly through C-H \cdots π ($d_{\text{D-H}}, 0.93 \text{ \AA}, d_{\text{D-A}}, 3.77 \text{ \AA}$) and C4-H \cdots O1 ($d_{\text{D-H}}, 0.93 \text{ \AA}, d_{\text{D-A}}, 3.95 \text{ \AA}, < \text{D-H}\cdots\text{A}, 174.23^\circ$) interaction is shown in figure 6(a) and (b), respectively. The layers are arranged such that the rings on each layer have C4-H \cdots O1 interactions and the rings from two adjacent sheets are positioned in the lattice so that two layers could move to closest proximity with least hindrance. Similar weak interactions and assembling are seen in **1b–1e**. This may be a reason that at 20 K when ring vibration and lattice vibration becomes negligible, weak interactions predominate, and depending on magnetic field, each layer can interact to show anomalous magnetic behavior. Thus, below 20 K a magnetic phase transition is observed.

3. Conclusion

In conclusion we have demonstrated the syntheses, characterization, and variable temperature magnetism of a series of 1-D coordination polymers of aromatic N-oxide

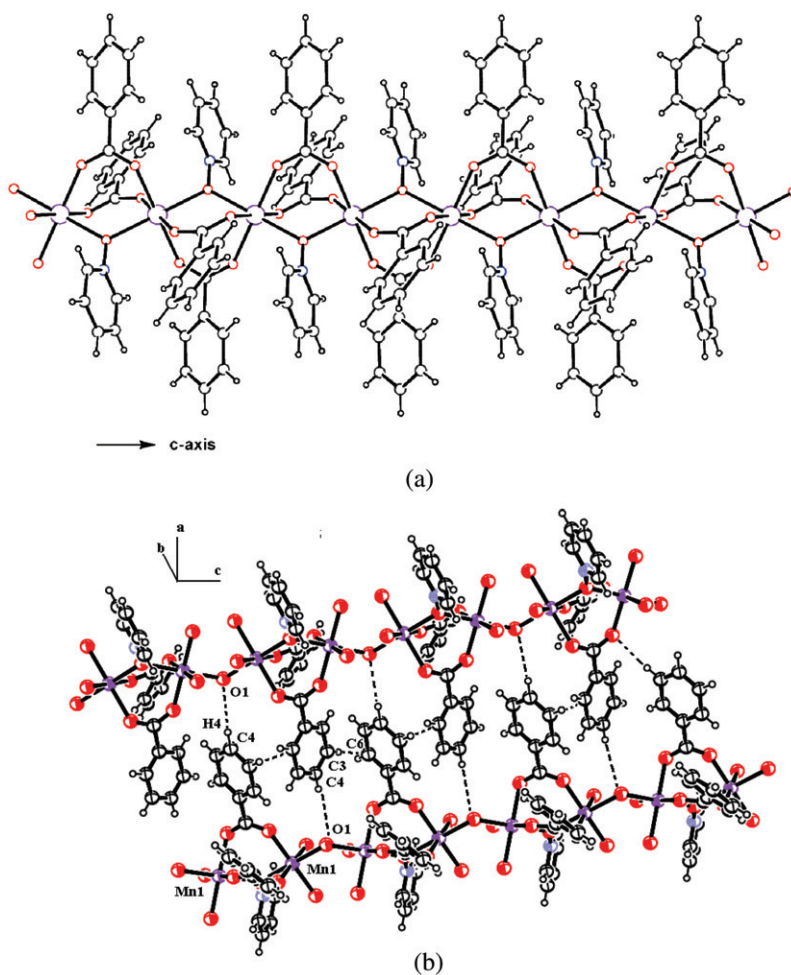


Figure 6. (a) Structure of 1-D polymer **1a** and (b) self-assembly formation through weak interactions.

bridged manganese(II). The coordination polymers described here are soluble in common solvents and may provide an avenue for developing advanced materials.

4. Experimental

4.1. Synthesis of the complexes

The synthesis of **1a** and **1b** were reported recently [5].

4.2. Synthesis of $[Mn(4-ClC_6H_4CO_2)_2(PyO)]_n$ (**1c**)

To a solution of 4-chlorobenzoic acid (2 mmol, 0.312 g) in methanol (15 mL) manganese acetate tetrahydrate (1 mmol, 0.245 g) was added and stirred for 10 min to obtain

a homogeneous solution. To this solution, PyO (3 mmol, 0.285 g) was added with constant stirring at room temperature with color change to yellow. A small amount (≈ 5 mL) of pyridine was added to dissolve the precipitate that appeared after addition of PyO. The clear solution thus obtained on standing gave white and yellow crystals. The white crystals were aqua-*bis*-pyridine *bis*-4-chlorobenzoato manganese(II) and the yellow crystals were coordination polymer (yield 70%). On re-dissolution in parent solution, white crystals converted to the coordination polymer. IR (KBr, cm^{-1}): 1597 (s), 1555 (s), 1474 (m), 1399 (s), 1218 (m), 771 (s). Molar conductance: $48.40 \text{ S cm}^2 \text{ mol}^{-1}$ in methanol. Elemental anal. calcd. for $[\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{MnNO}_5]_n$: C, 49.44; H, 2.82; found: C, 49.51; H, 2.85.

4.3. Synthesis of aqua-*bis*-pyridine *bis*-4-chlorobenzoato manganese(II) (2)

To a solution of 4-chlorobenzoic acid (2 mmol, 0.312 g) in methanol (15 mL) manganese acetate tetrahydrate (1 mmol, 0.245 g) was added and stirred for 10 min to obtain a homogeneous solution. To this solution pyridine (1 mL) was added and stirred for 1 h. The solution on standing gave **2** as a white solid. Yield of the pure crystalline complex was $\sim 35\%$. IR (KBr, cm^{-1}): 3402 (b), 1587 (s), 1526 (s), 1407 (m), 1093 (m), 775 (s). Molar conductance: $46.46 \text{ S cm}^2 \text{ mol}^{-1}$ in methanol. Elemental anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{MnN}_2\text{O}_5$: C, 53.11; H, 3.69; found: C, 53.13; H, 3.70.

4.4. Synthesis of $[\text{Mn}(4\text{-OHC}_6\text{H}_4\text{CO}_2)_2(\text{PyO})]_n$ (1d)

To a solution of 4-hydroxybenzoic acid (2 mmol, 0.276 g) in methanol (20 mL) $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1 mmol, 0.245 g) was added and stirred for 10 min. To this homogeneous solution PyO (3 mmol, 0.285 g) was added with constant stirring at room temperature; the color changed to yellow. A small amount of acetonitrile: water (1:1, ≈ 10 mL) was added to dissolve the precipitate that appeared after addition of PyO. Yellow crystals were collected after 3–4 days and dried in air. Yield of the pure crystalline complex was 26% (crude yield $> 70\%$). IR (KBr, cm^{-1}): 3299 (b), 1608 (m), 1591 (m), 1552 (s), 1478 (m), 1391 (s), 1341 (m), 1205 (m), 793 (m). Elemental anal. calcd. for $[\text{C}_{19}\text{H}_{15}\text{MnNO}_7]_n$: C, 53.79; H, 3.56; found: C, 53.85; H, 3.60.

4.5. Synthesis of $[\{\text{Mn}(2\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2)_2(\text{PyO})\} \cdot 2\text{H}_2\text{O}]_n$ (1e)

To a solution of 2-nitrobenzoic acid (2 mmol, 0.334 g) in methanol (20 mL) $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1 mmol, 0.245 g) was added and stirred for 10 min. and PyO (3 mmol, 0.285 g) was added with constant stirring at room temperature. The color of the solution changed to yellow. A small amount (≈ 2 mL) of water was added to dissolve the precipitate that appeared after addition of PyO. Yellow crystals were collected after 3 days and dried in air. Yield of the pure crystalline complex was 26% (crude yield $> 70\%$). IR (KBr, cm^{-1}): 3504 (b), 1602 (s), 1520 (s), 1477 (m), 1402 (s), 1346 (s), 1224 (m), 771 (m). Molar conductance: $55.96 \text{ S cm}^2 \text{ mol}^{-1}$ in methanol. Elemental anal. calcd. for $[\text{C}_{19}\text{H}_{15}\text{MnN}_3\text{O}_{11}]_n$: C, 44.16; H, 2.91; found: C, 44.23; H, 2.94.

Table 2. Crystallographic parameters of the manganese complexes.

Compound no.	1c	1d	1e	2
Formula	C ₁₉ H ₁₃ Cl ₂ MnNO ₅	C ₁₉ H ₁₅ MnNO ₇	C ₁₉ H ₁₅ MnN ₃ O ₁₁	C ₂₄ H ₂₀ Cl ₂ MnN ₂ O ₅
Mol. wt	461.14	424.26	516.28	542.26
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Cmcm</i>	<i>Pbcn</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>
Temperature (K)	296	296	296	296
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Unitcells dimensions (Å, °)				
<i>a</i>	27.0768(6)	16.3506(6)	14.4722(8)	15.1611(2)
<i>b</i>	9.6242(2)	13.7789(5)	7.4648(4)	5.92830(10)
<i>c</i>	7.47400(10)	7.4632(3)	7.4632(11)	27.7260(3)
α	90.00	90.00	90.00	90.00
β	90.00	90.00	90.865(3)	101.3380(10)
γ	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	1947.67(6)	1681.41(11)	2137.4(2)	2443.37(6)
<i>Z</i>	4	4	4	4
D _{Calc} (mg m ⁻³)	1.573	1.676	1.604	1.474
Abs. coeff. (mm ⁻¹)	0.983	0.831	0.686	0.797
Abs. correction	None	None	None	None
<i>F</i> (000)	932	868	1052	1108
Total no. of reflections	10291	16982	20041	25809
Reflections, <i>I</i> > 2σ(<i>I</i>)	1334	2079	4957	5725
Max. 2θ (°)	28.32	28.29	28.31	28.29
Ranges (<i>h, k, l</i>)	-36 ≤ <i>h</i> ≤ 36 -12 ≤ <i>k</i> ≤ 12 -9 ≤ <i>l</i> ≤ 9	-21 ≤ <i>h</i> ≤ 21 -18 ≤ <i>k</i> ≤ 17 -9 ≤ <i>l</i> ≤ 9	-18 ≤ <i>h</i> ≤ 19 -9 ≤ <i>k</i> ≤ 6 -26 ≤ <i>l</i> ≤ 26	-20 ≤ <i>h</i> ≤ 18 -7 ≤ <i>k</i> ≤ 7 -35 ≤ <i>l</i> ≤ 32
Complete to 2θ (%)	99.9	99.7	93.2	94.3
Refinement method	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²
Data/Restraints/Parameters	1334/0/80	2079/0/131	4957/0/315	5725/0/312
Goodness of fit (<i>F</i> ²)	1.135	1.025	1.039	1.022
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)], <i>R</i> ₁	0.0290	0.0351	0.0552	0.0393
<i>R</i> indices (all data), <i>R</i> ₁	0.0299	0.0517	0.0822	0.0586

4.6. X-ray crystallography

The X-ray single-crystal diffraction data were collected at 296 K with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT. The structures were solved by direct methods and refined by full-matrix least squares using SHELXTL software. All non-H atoms were refined in the anisotropic approximation against *F*² of all reflections. The H-atoms, except those attached to oxygen were placed at their calculated positions and refined in the isotropic approximation; those attached to oxygen were located in the difference Fourier maps and refined with isotropic displacement coefficients. The crystal data for the polymorphs are given in table 2.

4.7. Magnetic measurements

Temperature-dependent magnetization and magnetic hysteresis loops at various temperatures for the materials were examined by a superconducting quantum

interferometer device (SQUID, MPMS Quantum Design) magnetometer with an applied field up to ± 55 kOe; measurements were carried out from 5 to 300 K. Magnetic hysteresis loop measurement: -55 to $+55$ kOe at different temperatures.

4.8. ZFC curve

The samples were cooled to 5 from 300 K under zero external magnetic field. Once 5 K was reached, a constant magnetic field (1000 or 20 Oe) was applied and magnetization was measured as a function of temperature from 5 to 300 K.

4.9. FC curve

In this case, the samples were cooled to 5 from 300 K under constant external magnetic field (1000 or 20 Oe). Once 5 K was reached, magnetization was measured as a function of temperature from 5 to 300 K.

Supplementary materials

The crystallographic data files are deposited to the Cambridge Crystallographic Database and have CCDC numbers 661163, 661164, 665457, and 665458. Temperature-dependent ZFC and FC magnetization data of **1a** and **1b** measured at 20 and 1000 Oe are supplied.

Acknowledgments

The authors thank the Department of Science and Technology, New Delhi, India for financial support and SQUID measurements conducted at Tsukuba Magnetic Laboratory, National Institute for Materials Science, Sakura, Japan is greatly acknowledged.

References

- [1] (a) Y. Numata, K. Inoue, N. Baranov, M. Kurmoo, K. Kikuchi. *J. Am. Chem. Soc.*, **129**, 9902 (2007); (b) O. Kahn, J. Larionova, V. Jakhmi. *Chemistry: A Eur. J.*, **5**, 3443 (1999); (c) O. Kahn. *Phil. Trans. Royal Soc. London, Series A: Math. Phys. Eng. Sci.*, **357**, 3005 (1999); (d) O. Kahn, Y. Garcia, J.F. Letard, C. Mathoniere. *NATO ASI Series, Series C: Math. Phys. Sci.*, **518**, 127 (1999); (e) O. Kahn. *Chem. in Britain*, **35**, 24 (1999); (f) S.-Y. Fu, X.-M. Liu. In *Prog. Solid State Chem. Res.*, R.W. Buckley (ed.), Nova Science Publishers Inc, 165 (2007); (g) W.X. Xia, K. Tohara, Y. Murakami, D. Shindo, T. Ito, Y. Iwasaki, J. Tachibana. *IEEE Trans. Magnetics*, **42**, 3252 (2006).
- [2] (a) R.D. Carlin, L.J. De Jongh. *Chem. Rev.*, **86**, 659 (1986); (b) M. Kotowski, R. Marcec, V. Butkovic, A. Bakac, M. Orhanovic. *Eur. J. Inorg. Chem.*, **14**, 2894 (2006); (c) V. Laget, P. Rabu, C. Hornick, F. Romero, R. Ziessel, P. Turek, M. Drillon. *Mol. Cryst. Liq. Cryst. Sci. Tech. Sec. A: Mol. Cryst. Liq. Cryst.*, **305**, 291 (1997); (d) A. Misiolek, R. Huang, B. Kahr, J.E. Jackson. *Chem. Commun.*, **18**, 2119 (1996).

- [3] (a) D. Gatteschi, R. Sessoli. *Angew. Chem. Int. Ed. Eng.*, **42**, 2 (2003); (b) E.C. Sanudo, W. Wernsdorfer, K.A. Abboud, G. Christou. *Inorg. Chem.*, **43**, 4137 (2004); (c) A. Rodriguez-Dieguez, J. Cano, R. Kivekaes, A. Debdoubi, E. Colacio. *Inorg. Chem.*, **46**, 2503 (2007); (d) S. Tanase, F. Tuna, P. Guionneau, T. Maris, G. Rombaut, C. Mathoniere, M. Andruh, O. Kahn, J-P. Sutter. *Inorg. Chem.*, **42**, 1625 (2003); (e) W.-L. Liu, Y. Zou, C.-S. Lu, D.-B. Dang, Y.-Z. Li, Y.-G. Yao, Q.-J. Meng. *Polyhedron*, **23**, 2125 (2004); (f) U. Turpeinen, R. Hamalainen, J. Reedijk. *Polyhedron*, **6**, 1603 (1987); (g) P.D.W. Boyd, J.E. Davies, M. Gerloch. *Proc. Royal Soc. London, Series A: Math., Phys. Eng. Sci.*, **360**, 191 (1978); (h) R.W. Jotham, S.F.A. Kettle, J.A. Marks. *J. Chem. Soc., Dalton Trans.*, **3**, 428 (1972); (i) G. Christou, S.P. Perlepes, K. Folting, J.C. Huffman, R.J. Webb, D.N. Hendrickson. *Chem. Commun.*, **10**, 746 (1990).
- [4] (a) Y.-Z. Tang, X.-S. Wang, T. Zhou, R.-G. Xiong. *Cryst. Growth Des.*, **6**, 11 (2006); (b) K.S. Gavrilenko, S.V. Punin, O. Cador, S. Golhen, L. Ouahab, V.V. Pavlishchuk. *J. Am. Chem. Soc.*, **127**, 12246 (2005).
- [5] R. Sarma, A. Karmakar, J.B. Baruah. *Inorg. Chim. Acta*, **361**, 2081 (2008).
- [6] (a) S.-B. Yu, S.J. Lippard, I. Shweky, A. Bino. *Inorg. Chem.*, **31**, 3502 (1992); (b) A. Karmakar, K. Bania, A.M. Baruah, J.B. Baruah. *Inorg. Chem. Commun.*, **10**, 959 (2007).
- [7] (a) P.D.C. Dietzel, Y. Morita, R. Blom, H. Fjellvag. *Angew. Chem. Int. Ed. Eng.*, **44**, 6354 (2005); (b) I. Djerdj, D. Areon, Z. Jaglicic, M. Niederberger. *J. Phys. Chem.*, **111**, 3614 (2007).
- [8] R.E.E. Sesto, A.M. Atif, J.S. Miller. *Inorg. Chem.*, **39**, 4894 (2000).